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PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements relating to Ion-Exchange Resins

We, THE PERMUTIT COMPANY LIMITED, a British Company, of Permutit House, Gunnersbury Avenue, London, W.4, and THEODORE ROGER ERNEST KRESSMAN, a British subject, of the Company's address, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to ion-exchange resins produced by poly-condensation reactions. In practice these resins have always been formed into beds of granules through which the liquids flow. For many purposes, however, it would be advantageous to make the resins into rigid sheets, rods, discs or tubes, that is to say, to produce them in predetermined rigid shapes.

The reason why such shaped articles have not been made is that the resins have always cracked. When the gels initially formed are heated to complete the poly-condensation, the temperature attained must ordinarily be at least 90° C., and during the heating at this temperature evaporation with considerable shrinkage occurs and causes cracking and deformation of the mass. The shrunken mass expands and cracks still further upon subsequent immersion in water. In the standard process of manufacture this cracking is immaterial because in any event the mass is ground into small granules.

According to this invention ion-exchange resins made by poly-condensation to form a gel and subsequent heating to complete the poly-condensation are produced in the shape of sheets, rods, discs or tubes by carrying out the whole reaction under conditions such that water cannot escape and using a reaction mixture which contains solids and water in or substantially in the proportions required to make the product water-saturated. By "water-saturated" we mean that when the resin is immersed in water it will not swell appreciably, in contrast to resins produced by the standard process, which always take up water to compensate for that lost during the polymerising heating.

In order that no water can escape from the reaction system the container in which it is to take place must be closed, although the initial reaction before the formation of a gel may be effected under reflux, only the final heating being effected in the closed vessel.

In producing the resin, the amount of water required varies somewhat in accordance with the resin in question. When a resin is prepared under a given set of conditions of temperature and time the water required to saturate it will be fixed. If this is known accurately the water content of the reaction mixture can be adjusted accordingly. However, departures from the optimum water content thus ascertained can be allowed within limits, because the resin can undergo limited changes in volume without cracking.

When a resin has been chosen for use in the invention, it is a simple matter to make a small quantity of granules of the resin and ascertain their water content in the fully swollen state, and this gives an indication of the amount of water required, but it does not give the optimum figure. It seems that resins produced in closed vessels differ slightly in porosity from those produced by the standard process. The optimum figure for any given resin can be determined only by experiment, but in general the optimum water content is a little higher than that of the fully swollen or water-saturated resin of the same composition made by the standard process. We find that in typical cation-exchange resins of the kind in which the exchangeable cations are associated with carboxyl groups the water should be about 35% of the reaction mixture by weight, and in general the figure may vary between 30 and 40% without cracking of the resin occurring. In typical resins of the kind in which the exchangeable cations are associated with sulphonic groups the water content should be about 50% but may in general

vary between 40 and 55%. In typical weakly basic anion-exchange resins the water content should be about 48%, but may in general vary between 45 and 60%. Finally in typical strongly basic anion-exchange resins the water content of the reaction mixture should be about 47%, but may in general vary between 45 and 55%.

It is to be understood that the optimum water content of the reaction mixture varies with the nature and proportions of the constituents of the mixture, and the figures quoted above relate to typical mixtures and are given merely by way of indication. It is nearly always desirable to find the optimum figure for any given resin by experiment and then to use it, but it is not always possible to make the water content of the reaction mixture the optimum. Thus in the typical strongly basic anion-exchange resins the optimum water content so far as water saturation is concerned is 56%, but these resins will not form a gel at all if the water content is higher than 55%. To avoid all risk of the gel failing to form, we prefer to use a water content of 47% and thus to make a resin which will swell a little, but not enough to produce cracking, on immersion in water.

In calculating the ratio (or percentage) any formaldehyde (measured as CH_2O) or other non-solid constituent which becomes part of the solid gel is included in the solids. The amount of the water of condencsation is so small that it can be disregarded.

The simplest way of preventing water from escaping is, of course, to use a closed vessel throughout. However, effecting the initial stage of the reaction under reflux (which ensures that no water is lost) serves to keep to a minimum any small change in volume which might result from a possible difference in density between the liquid resin and the gel. Such heating under reflux is necessary when the constituents of the reaction mixture are such that a vigorous reaction occurs upon the initial application of heat and vapour is evolved, as if this occurred inside a closed vessel blow-holes would be formed in the resin. When a reflux process is used, the mixture while still liquid but viscous is transferred to a closed vessel and further heated to form the gel and complete the poly-condensation. It is to be understood that the evaporation which takes place in the standard process is not necessary to bring about the final poly-condensation; it is merely an inevitable result of heating the reaction mixture in an open vessel. Accordingly the reaction can be carried on in a closed vessel to prevent loss of the water without inhibiting the poly-condensation.

The products obtained by means of this invention are rigid but it is sometimes convenient to support them in or on porous materials. For instance, sheets supported on or in filter paper, sintered glass discs or porous unglazed porcelain may be made by impregnating the support with the viscous resin and effecting the solidification and poly-condensation in a sealed vessel. When the supporting material is omitted, the resin may be made in the form of a sheet, rod, disc or tube by carrying out the gel formation in a container of corresponding shape. For instance, a disc may be made in the bottom of a sealed glass cylinder, which is broken to remove the formed disc. A rod may be made in a sealed glass tube partly filled with the viscous liquid. Further, long rods or tubes may be made by a combination of extrusion and heating under conditions in which evaporation of the water is prevented. For example, the viscous resin mixture may be forced under slight pressure through a tube (or concentric tubes) heated to about 90° C. and arranged in a space which is either entirely closed or has a reflux arrangement on it to prevent loss of water. The resin solidifies continuously and then passes into another space, which is completely closed, the temperature being raised to that required to complete the poly-condensation, a temperature which varies with the resin but in general is of the order of 120° C.

When the product has an area which is large in comparison with its thickness, e.g. is an impregnated filter paper, it is advantageous to maintain the atmosphere in the closed vessel saturated with water vapour during the formation of the gel, and this may be done by putting a small quantity of water in the vessel while keeping it separate from the viscous liquid. This allows automatic adjustment of the water content to take place, since, if there is any small deficiency in the water content of the original reaction mixture, the resin will absorb water from the vapour space until it attains the equilibrium ratio of water to solid. In consequence, the water content of the reaction mixture may depart from the optimum, because any deficiency (which would cause shrinkage and so should be avoided) is compensated for, and a small excess is not harmful. However, in making a rod, for example, this saturation of the atmosphere with water vapour is of little value, because only one end of the rod is exposed to the water vapour. In such a case it is important to see that the water content of the reaction mixture is at the most very little different from the optimum figure determined for the resin in question.

The final product is porous (the pores being of molecular dimensions) and the pores are wholly occupied by liquid. This liquid is a solution in water of salts present in the reaction mixture and not included in the resin. For instance, in a resin formed from sulphonated phenol as an essential constituent

and condensed under alkaline conditions, an alkali metal sulphate (which in practice is sodium sulphate) is always present. This liquid must be removed by washing before the product can be used as formed or be subjected to an activating treatment to convert it to a desired ionic form. The concentration of salts in the liquid in the pores may be such that, on immersion of the product in washing water, osmotic pressure sufficient to produce internal cracks may be set up during the diffusion of the salts into the water. To prevent this the product may be initially immersed in a solution of sodium chloride or other salt having the same osmotic pressure and this solution may be gradually diluted and finally replaced by pure water, in which the product is washed until it is completely free from salts.

Some examples will now be given:—

EXAMPLE 1.

This is an example of the preparation of a rod of a sulphonic acid resin. 10 grams of phenol, 9 grams of sodium metabisulphite, 5 grams of sodium hydroxide, 18 cc. of 40% formaldehyde and 30 cc. of water were heated for 1 hour under reflux. The mixture was cooled and 16 grams of phenol, 28 cc. of water and 22 grams of paraformaldehyde were added, and the whole, the water content of which was 50%, was heated under reflux until the spontaneous reaction began. The heat was removed and the reaction allowed to proceed to completion. The mixture was then cooled, still under reflux, to yield a viscous liquid resin. A glass tube, 5 mm. in internal diameter and 30 cms. long, was sealed at one end and a quantity of the resin was poured into it until it formed a column 25 cms. long. The open end of the tube was then drawn out and sealed in a flame. The tube was then placed vertically in an oven at about 90° C. until the resin had solidified, whereupon the temperature was raised to 120° C. and kept there for 4 hours. The tube was cooled and opened and the rod of resin was removed and immediately immersed in water to prevent it drying out and distorting.

In the resin prepared as described in this example, the proportion of phenol can be increased or decreased to give a resin of lower or higher capacity, and generally the water will need to be proportionately decreased or increased.

EXAMPLE 2.

This is an example of the impregnation of a filter paper with a sulphonic acid resin. 10 grams of phenol and 10 grams of concentrated sulphuric acid were heated on a water bath for 30 minutes and then cooled, and 45 ccs. of water, 5 grams of sodium hydroxide, 10 grams of phenol and 10 grams of paraformaldehyde were added, the water content being 50%. The mixture was refluxed for 35 minutes and cooled whilst still under reflux to yield a viscous liquid resin. A strip of filter paper 12" long and 2" wide was dipped into the liquid resin, drained for 30 seconds, and then blotted between sheets of filter paper to remove the excess surface resin. The strip of paper impregnated with the resin was then introduced into a glass tube closed at both ends and containing a small open ampoule of water. The whole was placed in an oven at 100° C. for 6 hours. The paper was removed and washed with water.

EXAMPLE 3.

This is an example of the preparation of a disc of a weakly basic anion-exchange resin. 40 grams of phenol, 15 grams of sodium hydroxide and 40 grams of paraformaldehyde were dissolved in 20 cc. of water and heated under reflux until the spontaneous reaction began. This was allowed to go to completion and the mixture was then cooled. 50 grams of tetraethylene-pentamine were separately dissolved in 100 cc. of water and 30 cc. of 40% formaldehyde were added with stirring. The two solutions were mixed, the water content of the mixture being 48%, and heated under reflux for 30 minutes, and then cooled under reflux to yield a viscous liquid resin. A glass tube 25 mm. in diameter was sealed in a flame at one end with a flat sealed and a 3 mm. layer of resin poured in. About 50 mm. above the resin the glass tube was drawn out and sealed in the flame. The tube was stood on its flat bottom in a vertical position in an oven and heated to 95° C., until the resin solidified whereupon the temperature was raised to 110° C. for 5 hours. The tube was cooled and then opened and the disc of solid resin was removed and washed with water.

EXAMPLE 4.

This is an example of impregnating a cintered glass disc with a strongly basic anion resin. 20 cc. of acetone, 35 grams of paraformaldehyde, 45 cc. of water and 0.6 grams of sodium hydroxide were allowed to react spontaneously under reflux and then cooled. 34 grams of guanidine nitrate and 5 grams sodium hydroxide were dissolved as far as possible in 30 cc. water and the whole was added to the first solution, the water content of the mixture being 46%. The mixture was then heated under reflux, until a further spontaneous reaction had occurred, to yield a viscous liquid resin. A sintered glass disc of medium porosity, that known as "3," mounted at the end of a glass tube 10 mm. in diameter, was dipped just below the surface of the liquid resin so that the resin flowed through the holes in the disc and appeared on the upper side. The disc was immediately removed, the surplus resin was wiped away from the outside and the disc was supported within a small glass pressure vessel containing a small quantity of water. The vessel and its content were heated in an oven

at 90° C. for 2 hours and then at 110° C. for 5 hours. The vessel was cooled and opened, and the disc, now carrying the insoluble resin within its pores, was washed with water.

It has previously been proposed to make certain highly porous-condensation resins by carrying out the reactions under conditions such that water cannot escape from the reaction mixture, which is rich in water. Steps are also taken to prevent the resin from drying when it has been produced, since the presence of a high proportion of water is essential to give the final product good adsorptive power. Such processes will yield a solid resin mass which is subsequently ground up for use as granules. No directions are given to make the resin in the shape of a sheet, rod, tube or disc, and the solid resin mass formed as an intermediate product would be quite unsuitable for any of the purposes for which the products of the present invention are used.

Examples of these purposes are electrodialysis, the sheets according to the invention being used as the partitions, separation of large ions from small ions, and the measurement of ionic activities and mobilities. Again, filter papers impregnated with materials according to the invention may be used for the separation and detection of ions by paper chromatography. It may be pointed out here that in electrodialysis, for example, the ion exchange differs somewhat from that in a bed through which a liquid is passed for treatment. In such a bed the exchange is wholly of one ion (e.g. sodium) for another (e.g. calcium) whereas within the sheet of the invention there is exchange of one ion for another of the same kind, e.g. sodium for sodium; and whereas a bed must be regenerated from time to time, a sheet used in electrodialysis never needs regeneration.

What we claim is:—

1. A process in which an ion-exchange resin is produced in the shape of a sheet, rod, disc or tube with or without the use of a porous support by poly-condensation to form a gel and subsequent heating of the gel to complete the poly-condensation, the reaction mixture containing solids and water in or substantially in the proportion required to make the product water-saturated and the whole reaction being carried out under conditions such that water cannot escape.

2. A process in which a sheet, rod, disc or tube of an ion-exchange resin is made by poly-condensation to form a gel in a container of corresponding shape and subsequent heating of the gel to complete the poly-condensation, the reaction mixture containing solids and water in or substantially in the proportion required to make the product water-saturated and the whole reaction being carried out under conditions such that water cannot escape.

3. A process according to claim 1 or claim 2 in which the initial reaction before the formation of a gel is effected under reflux and the remainder of the reaction is effected in a closed vessel.

4. A process according to any of the preceding claims in which the atmosphere around the reaction mixture is maintained saturated with water vapour during the formation of the gel.

5. A process of manufacture in which ion-exchange takes place between a liquid and an ion-exchange resin in the shape of a sheet, rod, disc or tube produced by a process as claimed in any of the preceding claims.

6. Electro-dialysis processes in which the partitions are formed of sheets produced by a process as claimed in any of claims 1 to 4.

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PROVISIONAL SPECIFICATION

Improvements relating to Ion-Exchange Resins

We, THE PERMUTIT COMPANY LIMITED, a British Company, of Permutit House, Gunnersbury Avenue, London, W.4, and THEODORE ROGER ERNEST KRESSMAN, a British subject, of the Company's address, do hereby declare the nature of this invention to be as follows:—

This invention relates to ion-exchange resins produced by condensation reactions. At the present time these are used practically exclusively for the treatment of liquids, and in practice are always formed into beds of granules through which the liquids flow. For many purposes it would be advantageous to make the resins into rigid sheets, rods, discs, tubes and other shapes, that is to say, to produce them in stable bulk form. Hitherto this has been regarded as impossible, since the resins always crack. In their manufacture, in which condensation and polymerisation both take place, gels are formed. The reaction mass is heated to complete the polymerisation after the gel has formed, and during the heating evaporation with considerable shrinkage occurs and causes cracking and deformation of the mass. The shrunken mass expands and cracks still further upon subsequent immersion in water. As the mass is ground into small granules in the standard process, the fact that it is already cracked is immaterial.

According to this invention resins are produced in stable bulk form by using a reaction mixture which contains solids and water in a proportion which is the same as, or of the same order as, that in which they would be present in a resin of the same composition when it was fully swollen with water, and carrying out the whole reaction under conditions such that the water cannot escape. The evaporation which takes place in the usual process is not necessary to bring about polymerisation; it is merely an inevitable result of heating the reaction mixture in an open vessel. Accordingly the reaction can be carried on in a closed vessel to prevent loss of water without inhibiting the polymerisation.

The amount of water required varies somewhat in accordance with the resin in question. It is a simple matter to make a small quantity of granules of the desired resin and ascertain their water content in the fully swollen state, and then to adjust the ratio of water to solids in the reaction mixture accordingly in order to produce a stable bulk resin. In calculating the ratio any formaldehyde or other non-solid constituent which becomes part of the solid gel is included in the solids. We find that in typical cation-exchange resins of the kind in which the exchangeable cations are associated with carboxyl groups the water should be about 30% of the reaction mixture by weight; whereas in typical resins of the kind in which the exchangeable cations are associated with sulphonic groups the water content should be about 44%. In weakly basic anion-exchange resins the water content should be about 48%, and in strongly basic anion-exchange resins it should be about 56%.

The initial stage of the reaction (before the formation of the gel) need not be effected in a sealed vessel, but instead may be effected under reflux, which ensures that no water is lost. This serves to keep to a minimum any small change in volume which might result from a possible difference in density between the liquid resin and the gel. Such heating under reflux is necessary when the constituents of the reaction mixture are such that a vigorous reaction occurs upon the initial application of heat and vapour is evolved, as if this occurred inside a sealed vessel blow-holes would be formed. When a reflux process is used, the mixture while still liquid but viscous is transferred to a closed vessel and further heated to form the gel and complete the polymerisation.

It is advantageous to maintain the atmosphere in the closed vessel saturated with water vapour during the formation of the gel, and this may be done by putting a small quantity of water in the vessel while keeping it separate from the viscous liquid. This prevents the loss of water from the viscous resin or the gel into the air space above it in the closed vessel. It also compensates for any small deficiency in the water content of the original reaction mixture, since if there is such a deficiency the resin will absorb water from the vapour space until it attains the equilibrium ratio of water to solid. This compensation is very useful because a small excess of water is not very harmful but any deficiency causes shrinkage.

The shape of the final product is determined by the shape of the closed vessel. For instance, a disc may be made in the bottom of a sealed glass cylinder, which is broken to remove the formed disc. A rod may be made in a sealed glass tube partly filled with the viscous liquid. Long rods or tubes may be made by a combination of extrusion and heating under conditions in which evaporation of the water is prevented. For example, the viscous resin mixture may be forced under slight pressure through a tube (or concentric tubes) heated to about 90° C. and arranged in a space which is either entirely closed or has a reflux arrangement on it to prevent loss of water. The resin solidifies continuously and then passes into another space, which is completely closed, the temperature being raised to about 120° C. in this space.

The products are rigid but it is sometimes convenient to support them in or on porous materials. For instance, sheets supported on or in filter paper, sintered glass discs or porous unglazed porcelain, may be made by impregnating the support with the viscous resin and effecting the solidification and polymerisation in a sealed vessel.

The completely polymerised product is porous (the pores being of molecular dimensions) and the pores are wholly occupied by liquid. This liquid is a solution in water of salts present in the reaction mixture and not included in the resin. For instance, in a resin formed from sulphonated phenol as an essential constituent and condensed under alkaline conditions, an alkali metal sulphate (which in practice is sodium sulphate) is always present. This liquid must be removed by washing before the product can be used as formed or be subjected to an activating treatment to convert it to a desired ionic form. The concentration of salts in the liquid in the pores may be such that, on immersion of the product in washing water, osmotic pressure sufficient to produce internal cracks may be set up during the diffusion of the salts into the water. To prevent this the product may be initially immersed in a solution of sodium chloride or other salt having the same osmotic pressure and this solution may be gradually diluted and finally replaced by pure water, in which the product is washed until it is completely free from salts.

The products of this invention may be

used, for example, in electrodialysis, the separation of large ions from small ions, and the measurement of ionic activities and mobilities. Again, filter papers impregnated with materials according to the invention may be used for the separation and detection of ions by paper chromatography.

Dated this 2nd day of November, 1949.

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